Studies on Acetylene and its Derivatives. (IX) The Catalytic Conversion of Acetaldehyde to Acetone. (5) The Behaviors of the Derivatives of Acetaldehyde Catalyzed in the Vapor Phase by Some Metallic Oxides

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Studies on Acetylene and its Derivatives. (IX)

The Catalytic Conversion of Acetaldehyde to Acetone. (5) The Behaviors of the Derivatives of Acetaldehyde Catalyzed in the Vapor Phase by Some Metallic Oxides[1]

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This paper presents the behaviors of the derivatives of acetaldehyde —— ethylacetate, ethylalcohol, acetic acid, aldol, and isopropyl alcohol ——, or their aqueous solutions catalyzed in the vapor phase by ZnO, Fe_2O_3, or CaO, and the reaction mechanism of the formation of acetone from acetaldehyde and water.

On the basis of the obtained results, it seems most reasonable to assume that acetone is produced from acetaldehyde through the intermediate of ethylacetate.

INTRODUCTION

Previous works in this series[2),3)] have shown the good catalysts and the optimum reaction conditions in the synthesis of acetone from acetaldehyde and water in the vapor phase.

The present investigation was undertaken to research the reaction mechanism of the formation of acetone. For this purpose, the behaviors of the derivatives of acetaldehyde —— ethylacetate, ethylalcohol, acetic acid, aldol, and isopropyl alcohol —— or their aqueous solutions catalyzed in the vapor phase by ZnO, Fe_2O_3, or CaO have been studied.

EXPERIMENTAL

Apparatus, procedure, methods of preparation of catalysts, and **reaction conditions** were all the same as those described in the third paper of this series.[2)]

RESULTS

(1) Behaviors of Ethylacetate

The formed liquid and gas were analyzed according to the methods described in the second[4)] and third paper[3)] of this series, respectively. In Table 1 are shown the experimental results of ethylacetate.

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Table 1. Behaviors of Ethylacetate.
(Catalyst, 30 cc.; Reaction temperature, 400°C ; Ethylacetate, 25 cc.; Rate of dropping, 10 cc./hr.)

Catalyst	$CH_3COOC_2H_5$ (g./10 cc.)	$CH_3COOC_2H_5$ Total (g)	Conv. Ratio (%)	Products CH_3COOH (g.)	Products CH_3CHO (g.)	Products CH_3COCH_3 (g.)	Products C_2H_5OH (g.)	Yied of Acetone (%)	Gas Analysis (%) CO_2	Gas Analysis (%) C_nH_{2n}	Gas Analysis (%) CO	Gas Analysis (%) H_2	Gas Analysis (%) CH_4	H_2/CO_2
ZnO	9.040[a]	22.600	71.2	0.090	0	5.810	3.170	54.8	27.8	1.4	5.0	60.8	5.0	2.19
Fe_2O_3	〃	〃	73.4	0.036	0.401	3.465	3.897	31.6	65.4	5.1	3.1	12.7	13.7	0.19
CaO	〃	〃	94.1	0	0	3.633	8.911	25.8	12.7	0.8	4.9	72.9	8.7	—
ZnO	0.452[b]	1.130	73.9	0.004	0	0.280	0.193	50.9	36.2	0	5.4	58.4	0	1.61
Fe_2O_3	〃	〃	72.7	0.122	0.015	0.186	0.312	34.4	37.9	0.9	2.6	51.1	7.5	1.35
CaO	〃	〃	86.0	0	0	0.118	0.452	18.4	17.4	0	7.8	74.8	0	—

[a] Pure ethylacetate. [b] Aqueous ethylacetate.

Table 2. Behaviors of Ethylalcohol.
(Catalyst, 30 cc.; Reaction temperature, 400°C ; Rete of dropping, 10 cc./hr.)

Catalyst	C_2H_5OH (g./10 cc.)	C_2H_5OH Total (g.)	Conv. Ratio (%)	Products CH_3COOH (g.)	Products CH_3CHO (g.)	Products CH_3COCH_3 (g.)	Products C_2H_5OH (g.)	Yield of Acetone (%)	Gas Analysis (%) CO_2	Gas Analysis (%) C_nH_{2n}	Gas Analysis (%) CO	Gas Analysis (%) H_2	Gas Analysis (%) CH_4	H_2/CO_2
ZnO	7.779[a]	11.668/15 cc.	96.4	0.040	0	1.700	0.195	24.0	16.0	10.0	3.7	68.3	2.0	4.27
Fe_2O_3	〃	〃	99.3	0.030	0	2.150	0.225	29.4	17.3	4.6	4.3	66.4	7.4	3.84
CaO	〃	〃	21.8	0	0	0.820	0.225	51.4	0	0	0	100.0	0	—
ZnO	3.111[b]	7.778/25 cc.	97.8	0.050	0.090	1.965	0.200	41.5	18.3	2.1	1.7	75.0	2.9	4.10
Fe_2O_3	〃	〃	99.4	0.065	0.055	3.630	0.135	75.3	22.0	1.6	4.7	68.6	3.1	3.12
CaO	〃	〃	28.9	0	0	0.370	0.370	26.3	0	0	0	100.0	0	—

[a] Pure ethylalcohol. [b] Aqueous ethylalcohol.

The conversion ratio of pure or aqueous ethylacetate was about 70 % in either case of ZnO and Fe_2O_3 and about 90 % in case of CaO. With the catalyst of ZnO, Fe_2O_3, and CaO, the yields of acetone were 55 %, 32 %, and 26 %, respectively in case of pure ethylacetate, while 51 %, 34 %, and 18 % in case of an aqueous solution. With CaO, the yield of ethylalcohol was 77–80 % and markedly high as compared with other catalysts. These results agree with the low conversion ratio of ethylalcohol shown in the next paragraph (2) and the higher yield of ethylalcohol from acetaldehyde and water described in the fourth paper of this series. With ZnO, the ratio of H_2 to CO_2 in the formed gas was about 2 and with Fe_2O_3, increased from 0.19 (in using pure ethylacetate) to 1.35 (in using an aqueous solu tion), while with CaO, CO_2 being fixed on the catalyst, the contents of CO_2 were low.

From the above results, it is inferred that, in case of the catalyst of CaO, ethylacetate is the intermediate of acetone formation from acetaldehyde and water.

(2) Behaviors of Ethylalcohol

The produced liquid was analyzed by the method described in the second paper[4] of this series. The experimental results are given in Table 2.

The conversion ratio of pure or aqueous ethylalcohol was above 96 % in case of ZnO and Fe_2O_3 while only 20–30 % in case of CaO. With the catalyst of ZnO, Fe_2O_3, and CaO, the yields of acetone from pure ethylalcohol were 24 %, 29 %, and 51 %, but, from an aqueous solution, 41 %, 75 %, and 26 %, respectively.

In case of ZnO, the ratio of H_2 to CO_2 in the formed gas was 4 and in case of Fe_2O_3, a little lower than 4, but in case of CaO, H_2 was solely obtained.

On the basis of these data, it is inferred that acetaldehyde, from which acetone is formed, is produced by the dehydrogenation of ethylalcohol.

(3) Behaviors of Acetic Acid

The produced liquid was subjected to analysis according to the method described in the first paper[5] of this series. The experimental data are given in Table 3.

Table 3. Behaviors of Acetic acid.
(Catalyst, 30 cc.; Reaction temperature 400°C ; Acetic acid, 25 cc.; Rate of dropping, 10 cc./hr.)

Catalyst	Acetic acid		Conv. Ratio (%)	Acetone (g.)	Yield of Acetone (%)	Gas Analysis (%)				
	(g./10 cc.)	Total (g.)				CO_2	C_nH_{2n}	CO	H_2	CH_4
ZnO	10.485[a]	26.213	97.3	9.170	74.4	85.8	0	1.6	5.9	6.7
Fe_2O_3	〃	〃	90.8	10.255	89.1	94.8	0.6	1.5	0	3.1
CaO	〃	〃	95.6	4.982	41.1	23.1	0	7.7	0	69.2
ZnO	3.406[b]	8.515	98.3	2.881	71.1	91.2	0	3.3	0	5.5
Fe_2O_3	3.050[b]	7.625	81.5	2.617	87.0	80.1	0	4.4	0	15.5
CaO	3.209[b]	8.023	98.7	1.447	37.8	22.2	0	11.1	0	66.7

[a] Pure acetic acid. [b] Aqueous acetic acid.

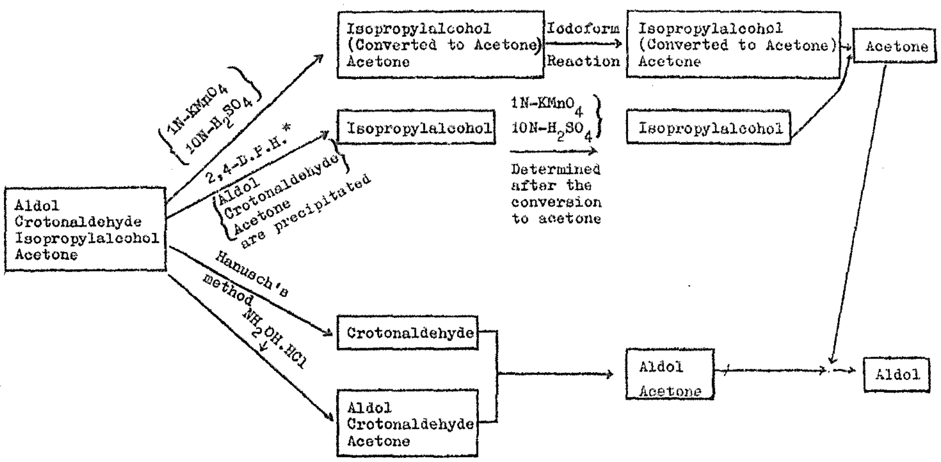
The conversion ratio of pure or aqueous acetic acid was above 90 % and the yields of acetone from pure acetic acid were 74 %, 89 %, and 41 % in case of ZnO, Fe_2O_3, and CaO while from an aqueous solution, 71 %, 87 %, and 38 %, respectively. In case of ZnO and Fe_2O_3, the formed gas almost consisted of CO_2 and this showed that acetone was produced by the decarboxylation of acetic acid.

In case of CaO, the contents of CH_4 were high. From this result one might conclude that acetic acid was decomposed to CH_4 and CO_2 and most of CO_2 were fixed on the catalyst as $CaCO_3$.

(4) **Behaviors of Aldol**

A 10 % aqueous solution of aldol was used. The produced crotonaldehyde, isopropyl alcohol, acetone and unreacted aldol were determined by the method shown in Fig. 1.

Fig. 1.



* 2.4-D.P.H : 2,4-Dinitrophenylhydrazine

The details of this analytical method will be reported in the other paper and the results of analysis by means of this method are as follows:

	Taken (mg.)	Found (mg.)	Accuracy* (%)	Corrected (mg.)
Aldol	30.6	27.8	90	30.9
Crotonaldehyde	30.4	24.1	80	30.0
Isopropylalcohol	32.1	26.4	80	33.0
Acetone	28.7	27.9	100	27.9

* Each accuracy was determined by the other experiment.

The experimental results are shown in Table 4.

With the catalyst of ZnO, Fe_2O_3, and CaO, the conversion ratio was 84 %, 83 %, and 43 % while the yields of acetone were 49 %, 44 %, and 17 %, respectively.

If isopropyl alcohol was the intermediate of acetone formation from aldol, the contents of CO in the formed gas should be high. But CO was not found, so that iroprôpyl alcohol was not the intermediate. The formation of acetone in these experiments may be due to the dissociation from aldol to acetaldehyde in an aqueous solution.

Table 4. Behaviors of Aldol.
(Catalyst, 15 cc.; Reaction temperature, 400°C ; Aldol, 25 cc.;
Rate of dropping, 10 cc./hr.)

Catalyst	Aldol		Conv. Ratio (%)	Products			Yield of Acetone (%)	Gas Analysis (%)					H_2/CO_2
	(g./10 cc.)	Total (g.)		CR.A[a] (g.)	Acetone (g.)	I.P.A.[b] (g.)		CO_2	CnH_2n	CO	H_2	CH_4	
ZnO	1.177[c]	2.943	84.4	0.339	0.795	0.188	48.5	34.3	3.5	1.0	59.2	0	1.72
Fe_2O_3	〃	〃	83.2	0.588	0.705	0.177	43.6	54.6	7.0	0	38.4	0	0.70
CaO	〃	〃	42.8	0.540	0.144	0.150	17.3	22.2	0	0	77.8	0	—

[a] Crotonaldehyde. [b] Isopropylalcohol. [c] Aqueous aldol.

(5) Behaviors of Isopropyl Alcohol

The produced acetone and the unreacted isopropyl alcohol were analyzed respectively by the method of using NH_2OH. HCl described in the first paper[7] of this series and the same method as that of the analysis of ethylalcohol with $K_2Cr_2O_7$ described in the second paper[1]. The experimental results are given in Table V.

Table 5. Behaviors of Isopropylalcohol.
(Catalyst, 30 cc.; Reaction temperature, 400°C ; Isopropylalcohol, 25 cc.;
Rate of dropping, 10 cc./hr.)

Catalyst	Isopropylalcohol		Conv. Ratio (%)	Acetone (g.)	Yield of Acetone (%)	Gas Analysis (%)				
	(g./10 cc.)	Total (g.)				CO_2	CnH_2n	CO	H_2	CH_4
ZnO	8.090[a]	20.225	80.2	9.403	60.0	2.9	16.3	1.1	79.7	0
Fe_2O_3	〃	〃	75.2	7.167	48.8	7.9	9.2	1.7	76.0	5.2
CaO	〃	〃	24.4	4.542	95.1	0.2	2.2	0	97.6	0
ZnO	2.720[b]	6.800	89.4	2.518	62.9	8.8	11.1	0	80.1	0
Fe_2O_3	2.832[b]	7.080	73.9	3.360	66.4	4.5	4.0	2.3	81.5	7.7
CaO	2.720[b]	6.800	—	2.345	—	0	0.6	0.6	98.8	0

[a] Pure isopropylalcohol. [b] Aqueous isopropylalcohol.

With the catalyst of ZnO, Fe_2O_3, and CaO, the yield of acetone from pure or aqueous isopropyl alcohol was above 50 %. The formed gas almost consisted of H_2 and this showed that acetone was produced by the dehydrogenation of isopropyl alcohol. Therefore, if isopropyl alcohol was formed from aldol, acetone should be produced.

CONSIDERATION

With the catalyst of ZnO, Fe_2O_3, and CaO, the reaction mechanism of acetone formation from acetaldehyde is anticipated as follows:

(I)[6),7)] (a) With pure acetaldehyde[5)]

$$4CH_3CHO \longrightarrow 2CH_3COOC_2H_5$$
$$2CH_3COOC_2H_5 \longrightarrow CH_3COCH_3 + CO_2 + C_2H_4 + C_2H_5OH$$

(b) With aqueous acetaldehyde

$$4CH_3CHO \longrightarrow 2CH_3COOC_2H_5$$
$$2CH_3COOC_2H_5 + 2H_2O \longrightarrow 2CH_3COOH + 2C_2H_5OH$$
$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$
$$2C_2H_5OH \longrightarrow 2CH_3CHO + 2H_2$$
$$\overline{2CH_3CHO + H_2O \longrightarrow CH_3COCH_3 + 2H_2 + CO_2}$$

(II)[9),10),11),12)]

$$2CH_3CHO + 2H_2O \longrightarrow 2CH_3COOH + 2H_2$$
$$2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$
$$\overline{2CH_3CHO + H_2O \longrightarrow CH_3COCH_3 + 2H_2 + CO_2}$$

(III)[6)]

$$2CH_3CHO \longrightarrow CH_3.CH(OH).CH_2.CHO$$
$$CH_3.CH(OH).CH_2.CHO \longrightarrow CH_3.CH(OH).CH_3 + CO$$
$$CH_3.CH(OH).CH_3 \longrightarrow CH_3COCH_3 + H_2$$
$$\overline{2CH_3CHO \longrightarrow CH_3COCH_3 + H_2 + CO}$$

In mechanism I, the intermediate of acetone formation is ethylacetate, in mechanism II, acetic acid or its metallic salt, and in mechanism III, isopropyl alcohol.

But, from the experimental results of aldol (in paragraph (4) of this paper), it was found that isopropyl alcohol was not the intermediate. Therefore, mechanism III was denied.

In mechanism II, the presence of water is necessary for the formation of acetic acid. With mechanism II, the formation of acetone from pure acetaldehyde (in the fourth paper[3)] of this series) and from pure ethylalcohol (in paragraph (2) of this paper) can not be interpreted. But when the aqueous acetaldehyde is used, acetic acid or its salt may be the intermediate.

While, with mechanism I —— the intermediate is ethylacetate —— the formation of acetone from pure or aqueous acetaldehyde can be explained reasonably, and the formation of ethylalcohol, with the catalyst of CaO, can also be interpreted. Therefore, it seems most probable that acetone is formed from acetaldehyde through the intermediate of ethylacetate.

SUMMARY

(1) The behaviors of the derivatives of acetaldehyde —— ethylacetate, ethylalcohol, acetic acid, aldol and isopropyl alcohol which are anticipated as the intermediates of acetone formation from pure or aqueous acetaldehyde catalyzed in the

vapor phase by ZnO, Fe_2O_3, or CaO —— have been investigated.

(2) On the basis of the experimental results, the reaction mechanism of acetone formation from acetaldehyde was considered and it seems most probable that acetone is formed through the intermediate of ethylacetate.

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